Carbon Based Superconductors

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Abstract

We review the characteristics of some carbon based novel superconductors which emerged in the past two decades since the discovery of superconductivity in the high-T_c oxocuprates. In particular, we summarize the properties of ternary layered carbide halides of the rare rarth metals with composition $RE_2C_2X_2$ (RE = Y, La; X=Cl, Br, I) and of the rare earth di- and sesquicarbides, YC_2, LaC_2 and La_2C_3. Finally, we briefly discuss the properties of the recently discovered Ca and Yb intercalated graphite superconductors, CaC_6 and YbC_6.

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I. INTRODUCTION

The discovery of high-T_c superconductivity by Bednorz and Müller[1] in 1986 marks the beginning of a period of a vivid search for - chemically and physically partly extremely complex - new oxocuprates and for theoretical approaches to understand their puzzling properties, quite a few of which remained controversial even until today. The advent of this completely unexpected class of new superconductors also revived the interest in more conventional - 'low-T_c' - superconductors. In due course, a number of new systems were found, and already known superconductors were reinvestigated with improved and refined experimental and theoretical tools. These activities led to surprising new discoveries as that of the 40 K superconductor MgB_2 by Nagamatsu *et al.*[2] Apart from its T_c, MgB_2 is special primarily for two reasons: Compared *e.g.* to the high-T_c oxocuprates its crystal structure is of remarkable simplicity allowing electronic and phononic structure calculations of high precision, and MgB_2 is the first system for which *multigap* superconductivity has independently been evidenced by several experimental techniques.[3,4,5]

Until the discovery of MgB_2, doped fullerenes had shown the highest T_c values after the high-T_c oxocuprates. With large enough quantities of purified C_{60} available,[6] Hebard *et al.* prepared superconductors with a T_c of 18 K by doping polycrystalline C_{60} and C_{60} films with alkali metals.[7] Subsequently, by adjusting the separation of the C_{60} molecules using a proper composition of different alkali metals, T_c's up to $\sim$33 K were reached.[8]

Superconductivity in doped fullerenes also redraw attention to carbon based superconductors in general. Especially, binary and quasibinary transition metal carbides have a long history in showing T_c's which were among the highest found before the discovery of the high-T_c oxocuprates.[9] Later borocarbides of composition REM_2B_2C, with RE = Y or Lu and M = Ni or Pd, with T_c's up to 22 K attracted considerable interest.[10,11]

Superconductivity in graphite intercalation compounds (GICs) is another early field of research which recently was revived. The discovery of superconducting GICs dates back to the pioneering work of Bernd Matthias' group in the 1960's, however, the T_c's of these early GICs remained well below 1 K.[12,13] Subsequently, the T_c's of alkali metal intercalated GICs could be raised by intercalation under pressure with *e.g.* Li and Na, but T_c did not significantly exceed the boiling point of liquid helium.[14] It was not until recently that T_c of the GICs could be significantly enhanced by intercalating divalent alkaline earth metals like

Ca and Yb.[15]

Finally, after graphite and C_{60}, diamond was also converted into a superconductor by hole doping induced by a substitution of about 3% B into C sites. Ekimov *et al.* showed that such a boron-doped diamond is a bulk, type-II superconductor below $T_c \sim 4$ K with superconductivity surviving in a magnetic field up to $H_{c2}(0) \geq 3.5$ T.[16]

In our search for complex metal-rich rare earth halides we found a series of new superconducting layered carbide halides of the rare earth metals with T_c's up to ∼10 K.[17,18,19] For a deeper understanding of the chemistry and physics of these we in turn reinvestigated also the properties of binary dicarbides and sesquicarbides of composition REC_2 and RE_2C_3, with R = Y,La. Superconductivity in binary carbides of rare earth metals had been an intensively investigated topic in the sixties and seventies of the last century. In this family of compounds T_c values peaked with $(Y_{0.7}Th_{0.3})_2C_3$ at 17 K.[20]

Superconductivity in rare earth metal sesquicarbides recently regained considerable attention after the reports by Amano *et al.* and Nakane *et al.* about the successful synthesis of binary Y_2C_3 under high pressure conditions (∼5 GPa).[21,22] The reported T_c's reached 18 K and the upper critical field exceeded 30 T. In the following we will summarize some of the characteristic properties of the ternary layered rare earth metal carbide halides and the binary di- and sesquicarbides. We conclude with some remarks on our results on the recently discovered alkali earth GICs.

II. SUPERCONDUCTIVITY IN RARE EARTH CARBIDE HALIDES AND RARE EARTH CARBIDES

A. Ternary Layered Cabide Halides of the Rare Earth Metals

The carbide halides of the rare earth metals, $RE_2C_2X_2$ (X = Cl, Br, I and RE being a rare-earth metal) crystallize with layered structures which contain double layers of close-packed metal atoms sandwiched by layers of halogen atoms to form X-RE-C_2-RE-X slabs as elementary building blocks. These connect via van der Waals forces in stacks along the crystallographic *c*-axis. Different stacking sequences (1s and 3s stacking variants) have been found. The carbon atoms form C-C dumbbells which occupy the octahedral voids in the close-packed metal atom doublelayers (cf. Fig. 1).[23,24]

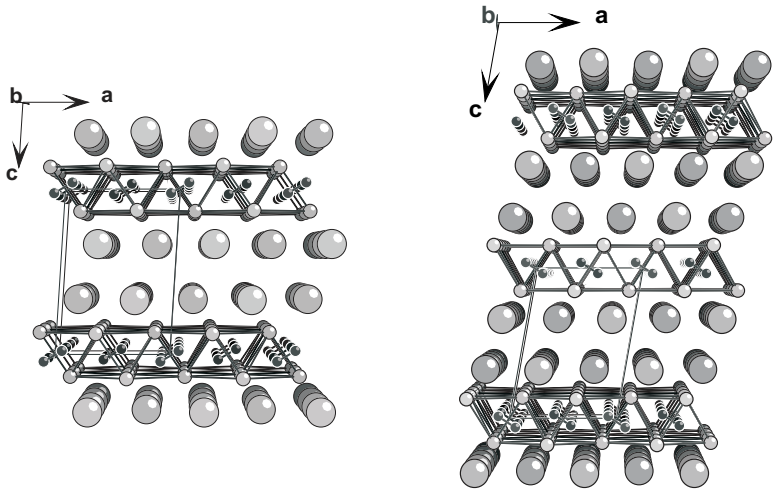

FIG. 1: (left) Crystal structure of $Y_2C_2I_2$ (1s stacking variant) and (right) crystal structure of $Y_2C_2Br_2$ (3s stacking variant) projected along [010] with the unit cells outlined. C, Y, and (I,Br) atoms are displayed with increasing size.

Compounds containing the nonmagnetic rare-earth metals Y and La are superconductors (Fig. 2). The maximum T_c of 11.6 K which was achieved by adjusting the composition in the quasi-ternary phases $Y_2C_2(X,X')_2$.[18] The variation of $T_c(x)$ across the transition of the 3s and the 1s stacking variant indicating that superconductivity is essentially a property of the configuration of an individual X-RE-C_2-RE-X slab rather than of the stacking details in the crystal structure. The transition temperatures of all known superconducting phases $RE_2C_2X_2$ are compiled in Table I.

compound	T_c (K)	$\mu_0 H_{c2}$ (T)	reference
$Y_2C_2Cl_2$	2.3	-	18
$Y_2C_2Br_2$	5.04	3	18,19,25
$Y_2C_2I_2$	10.04	12	18,25,26,27
$Y_2C_2Br_{0.5}I_{1.5}$	11.6	-	18
$La_2C_2Br_2$	7.03	-	28
$La_2C_2I_2$	1.72	-	28

TABLE I: Transition temperatures and upper critical fields, $\mu_0 H_{c2}$, of the known superconducting phases $RE_2C_2X_2$ (RE = Y, La; X=Cl, Br, I)

The heat capacity of $Y_2C_2I_2$ shows a sharp anomaly, however with a jump height $\Delta C_P(T_C)/\gamma T_C \approx 2$ which is considerably larger than the value 1.43 expected from weak coupling BCS theory.[19,26] A fit of the heat capacity anomaly with the empirical α-model[29] indicates strong coupling with $2\Delta(0)/k_B T_C \approx 4.2$, the superconducting gap being enhanced by about 20 % over the BCS value, similar to the σ - gap in MgB_2[30]. There is, however, no indication from the temperature dependence of the heat capacity anomaly for a multiple gap scenario. Using approximate equations for strong coupling superconductors which relate $2\Delta(0)/k_B T_C$ and $\Delta C_P(T_C)/\gamma T_C$ to the logarithmic average over the phonon frequencies ω_{ln}[31,32] one estimates the typical phonon frequency range for $Y_2C_2I_2$ to be $\sim$80 - 100 cm^{-1}. In this range A_g modes have been discerned by Raman spectroscopy in which Y and halogen atoms vibrate in-phase parallel and perpendicular to the layers.[33,35]

C stretching and tilting vibrations have considerably higher energies, and their role for electron-phonon coupling, particularly in the case of the tilting modes, could be important.[36] The electronic structure in close neighborhood to the Fermi energy, E_F, is characterized by bands of low dispersion which are reminiscent of the quasimolecular character of the HOMO and LUMO orbitals of an isolated C-C dumbbell.[35,37] These together with highly

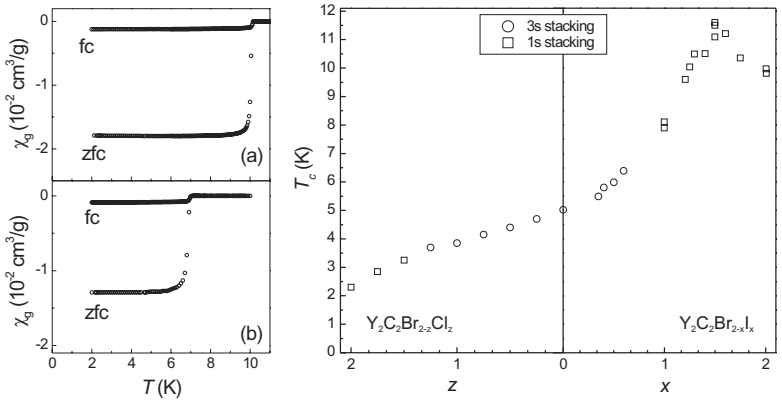

FIG. 2: (left) field-cooled (fc) and zero field-cooled (zfc) magnetic susceptibilities of (a) $Y_2C_2I_2$ (after ref.[26]) and (b) $La_2C_2Br_2$ (after ref.[28]). (right) T_c's of a series of quasiternary mixtures of $Y_2C_2Br_{2-x}I_x$ and $Y_2C_2Br_{2-z}Cl_z$. Different stacking variants of the compounds are indicated by different symbols (after ref.[18]).

dispersive bands establish a flat/steep band scenario which in our view is a prerequisite of superconductivity in a more general sense.[34]

The low-dispersive bands give rise to two peaks in the electronic density of states, DOS, each about 100 meV above and below the Fermi energy which enclose a 'pseudogap' at E_F.[35,37] Deviations from the linear temperature dependence of the Korringa relaxation of ^{13}C nuclei probed by ^{13}C NMR are a clear manifestation for the proposed structure in the DOS close to E_F.[38]

The electronic structure and the dispersion of the bands in the vicinity of E_F is very sensitive to slight structural variations and can be very effectively tuned e.g. by hydrostatic pressure to increase the DOS and maximize T_c.[39] When hydrostatic pressure is applied to $Y_2C_2I_2$ T_c increases, and a maximum of about 11.7 K is reached at 2 GPa, similar to the maximum T_c found in the quasi-ternary mixtures.[27,39,40] The increase of T_c with pressure $Y_2C_2I_2$ and also $La_2C_2Br_2$ is remarkable and parallels the findings in observed for the Hg based oxocuprates but also for fcc-La for which similar values for the relative increase $1/T_c \cdot dT_c / dP$, have been detected.[41,42]

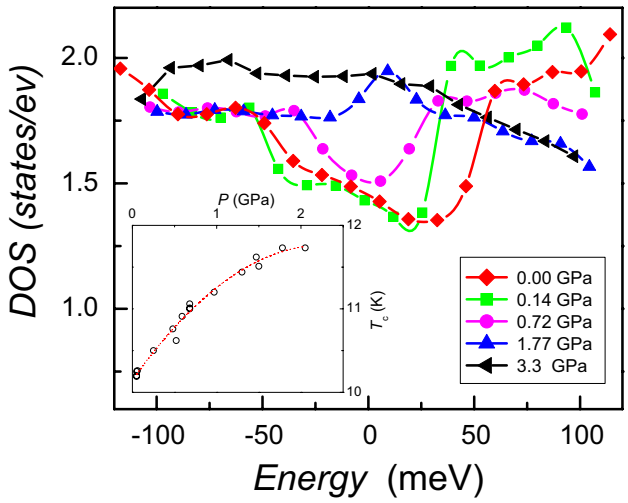

FIG. 3: Electronic density of states, DOS, of $Y_2C_2I_2$ in the close vicinity to E_F. The inset shows the pressure dependence of T_c of $Y_2C_2I_2$. The dotted line is a guide to the eye (after ref. [39,40]).

B. Binary Dicarbides and Sesquicarbides of the Rare Earth Metals

YC_2 crystallizes with the body centered tetragonal CaC_2 structure type (Fig. 4) with C-C dumbbells centering Y metal atom octahedra which are slightly elongated along [001].[43] YC_2 had been found to be a superconductor with a $T_c \sim 3.88$ K.[44] Proper heat treatment of stoichiometric YC_2 samples results in superconductors with a sharp transition and onset T_c's up to 4.02(5) K , somewhat increased over those previously reported.[45,46] LaC_2 shows a T_c of about 1.6 K.[44]

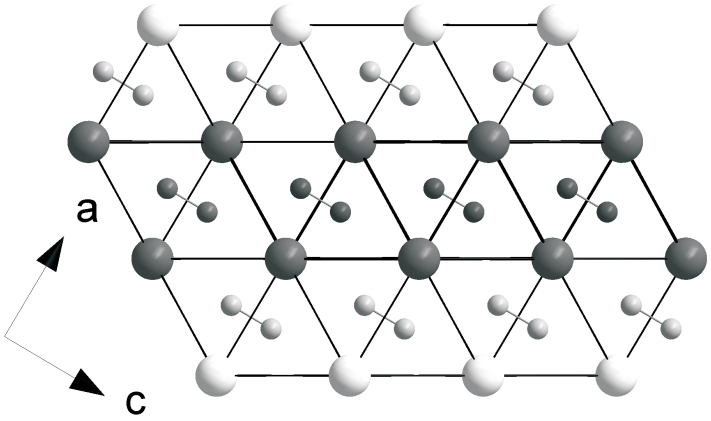

FIG. 4: Crystal structure of YC_2 along [0 1 0]. Y and C atoms are drawn with decreasing size. An Y - C_2 - Y doublelayer as found in the ternary carbide halides of the rare earths metals, $RE_2C_2X_2$ (RE = Y, La; X = Cl, Br, I), is highlighted in dark grey.

Heat capacity measurements (Fig.5) nicely reveal the anomaly at the transition to superconductivity which follows closely the BCS weak-coupling predictions but already indicate significantly decreased critical fields as compared to those of the layered carbide halides.[25]

Electronic structure calculations for YC_2 reveal strongly dispersive bands in planes perpendicular to the c - direction originating from Y $d_{x^2-y^2}$ orbitals and also strongly dispersive bands in the c - direction emerging from combinations of Y d_{xz}, d_{yz}, and C p_x, p_y orbitals.[45] As a consequence the electronic density of states close to the Fermi level is to a large extent featureless with a slight positive slope. Doping with Th or Ca (10 % to 20 %) decreases T_c.[45]

As compared to the layered yttrium carbide halides, the critical fields of YC_2 (< 0.1 T, cf.

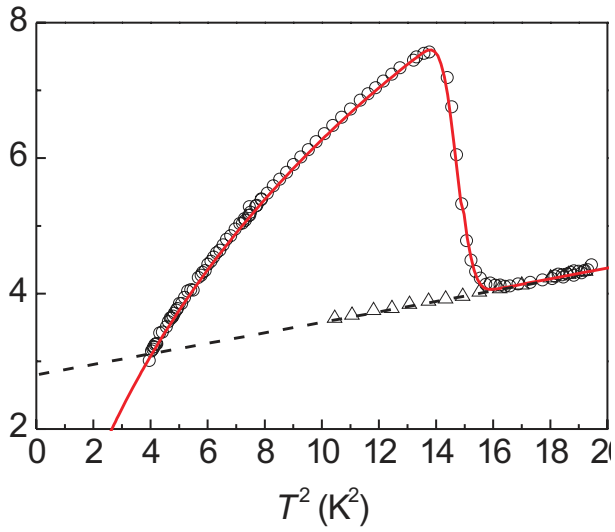

FIG. 5: Superconducting anomaly in the heat capacity of YC_2 (B_{ext}=0, ∘). The normal state △ has been reached by applying an exernal field of 0.4 T (after ref.[45]). The (red) solid line represents a fit to the predictions of the BCS theory with a slight smearing of T_c being included.

Fig.6 and Table I) are reduced by up to two orders of magnitude . The significant difference in the upper critical fields between the layered carbide halides and the dicarbides as well as the marked increase in the anisotropy of the coherence lengths ($\xi_{\parallel}/\xi_{\perp} \approx 5$,[25]) supports Ginzburg's suggestion that from the point of view of possibilities to enhance T_c promising materials are layered materials and dielectric-metal-dielectric sandwich structures.[47,48] In fact, by comparing the crystal structures of the dicarbides and the carbide halides of the rare earths (Figs. 1 and 4) one realizes that the R-C_2-R doublelayers carrying the superconductivity in the ternary carbide halides can be considered as sections of the three dimensional structure of the dicarbides which are sandwiched by dielectric halogen layers. In this respect, the dicarbides and the carbide halides of the rare earth metals are interesting examples to test Ginzburg's conjecture.

La_2C_3 (like Y_2C_3) crystallizes with the cubic Pu_2C_3 structure in the space group $I\bar{4}3d$

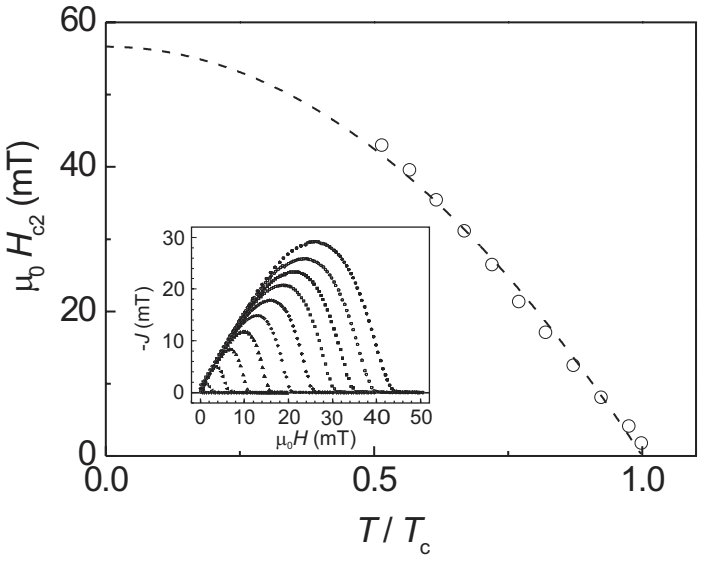

FIG. 6: Upper critical field, $\mu_0 H_{c2}$, determined from the isothermal magnetization measured of a spherical sample of YC_2. The inset displays the isothermal magnetizations measured at constant temperatures of 2K, 2.2K, ..., 3.8K, 4K, in decreasing order (after ref.[25]).

which belongs to the tetrahedral crystallographic class T_d with no center of symmetry.[49] The structure contains C–C dumbbells in a distorted dodecahedral coordination ('bisphenoid') formed by 8 La atoms (cf. Fig. 7). For a more detailed discussion of the problems of C deficiency and the problem of the aniostropy of the thermal ellipsoids of the C atoms see ref. [57]. A recent study of the crystal structure up to high pressures could not detect any structural phase transitions up to 30 GPa.[50]

In non-centrosymmetric systems with significant spin-orbit coupling superconducting order parameters of different parity can be mixed. A recent system which attracted particular interest in this respect, is the heavy fermion superconductor $CePt_3Si$ which shows unconventional properties, as *e.g.* antiferromagnetism and superconductivity at $T_N \sim 2.2$ K and $T_c \sim 0.75$ K, respectively, and an upper critical field which considerably exceeds the paramagnetic limit.[51] With no $4f$ electrons present and the high atomic mass of La (as compared to Y) La_2C_3 is therefore an interesting system to study the effects of non-centrosymmetry on superconductivity. Possible multi-gap superconductivity is another interesting issue which has been proposed for Th doped Y_2C_3 and La_2C_3.[63] Recently, Harada *et al.* from ^{13}C NMR measurements reported multi-gap superconductivity for Y_2C_3.[64]

In contrast to Y_2C_3 which requires high-pressure synthesis methods[21,22], samples of La_2C_3

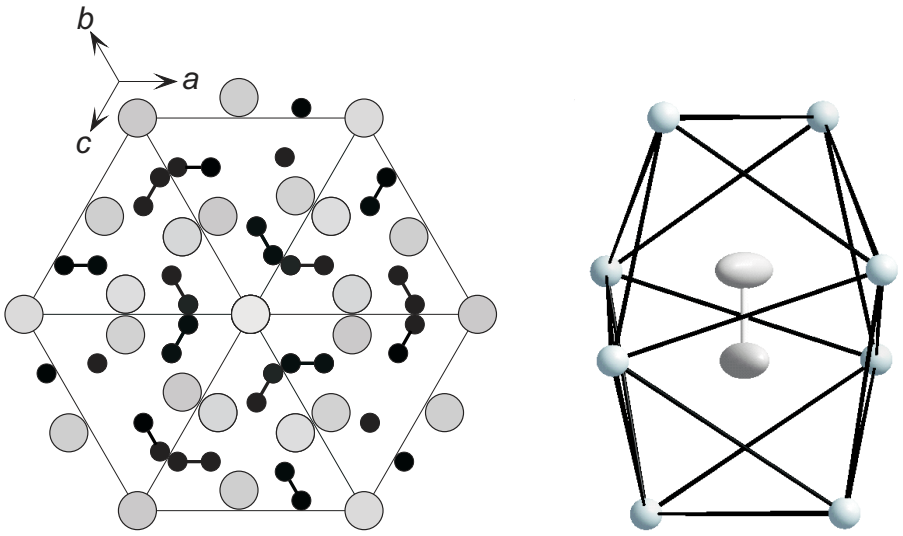

FIG. 7: Crystal structure of La_2C_3 projected along [1 1 1] (after ref. [46]. (left) Unit cell with La atoms indicated by the large spheres. (right) La atom environment of a C - C dumbbell. The thermal ellipsoids of the C atoms are shown.

are readily accessible by arc-melting of the constituents. Early on, La_2C_3 was reported to have a T_c of $\sim$ 11 K.[52,53,54] Subsequently, it has been shown that these samples were not stoichiometric, as anticipated, but exhibit a range of homogeneity from 45.2% to 60.2% atom-% carbon content.[46,55,56] Investigations of a series of samples $La_2C_{3-\delta}$ with $0.3 \geq \delta \geq 0$ indicate a separation into two superconducting phases with rather sharp T_c's of $\sim$ 6 K and 13.3 - 13.4 K (Fig. 8). The high T_c values are attributed to stoichiometric La_2C_3, viz. negligible C deficiency, which was assured individually for the samples by neutron powder diffraction.[26,57,59]

Our electronic structure calculations show a splitting of the bands near E_F indicating that the spin degeneracy is lifted due to a sizable spin-orbit coupling in addition to the non-centrosymmetry in the structure.[59] However, the band splitting in La_2C_3 is much smaller than those found for other non-centrosymmetric superconductors like $CePt_3Si$, Li_2Pt_3B or $Cd_2Re_2O_7$.[60,61,62] For Li_2Pd_3B, another non-centrosymetric superconductor, where the band splitting is comparable with that of La_2C_3, conventional BCS type behavior with an isotropic

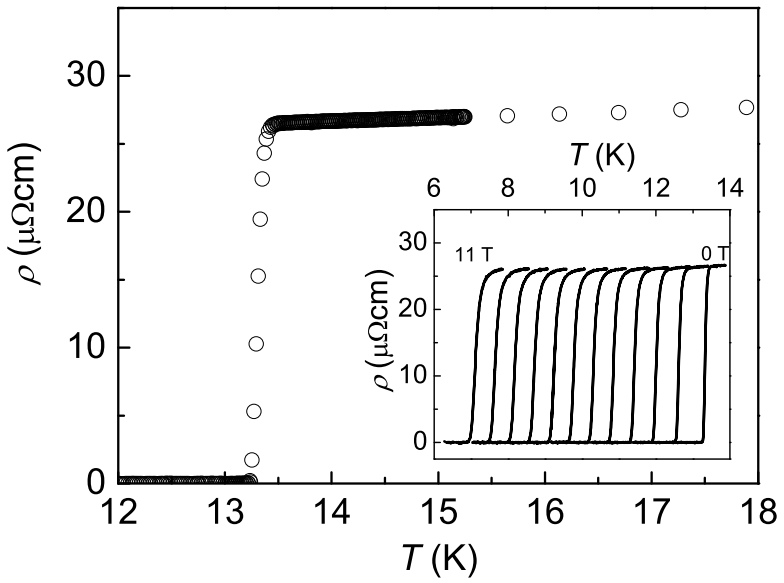

FIG. 8: Low temperature electrical resistivity of La_2C_3 showing the superconducting transition at 13.4 K. The inset demonstrates the decrease of the superconducting transition with external magnetic fields ranging from 0 T, 1 T, ..., 11 T.

superconducting gap has been established via μSR experiments.[65] Based on our heat capacity measurements we similarly conclude that La_2C_3 is a system with strong electron-phonon coupling with a single gap of isotropic *s*-wave symmetry.

The upper critical field was determined by various methods and reaches a value of ∼20 T at $T \rightarrow 0$ K (Fig. 9). $\mu_0 H_{c2}$ is clearly enhanced over the Werthamer-Helfand- Hohenberg predictions,[66] but it does not exceed the paramagnetic limit. Therefore, even though band splitting effects due the non-centrosymmetric structure are present, they appear to be not significant in case of La_2C_3.

III. SUPERCONDUCTIVITY IN ALKALINE EARTH INTERCALATED GRAPHITE

The recent discovery of superconductivity in Ca- and Yb - intercalated graphite has refocused considerable interest onto graphite intercalated compounds (GICs).[15,67] The super-

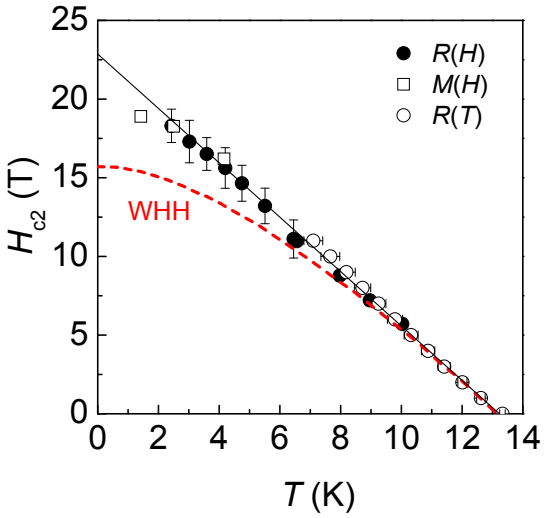

FIG. 9: Upper critical field of La_2C_3 determined by various experimental methods, magnetoresistance ($R(H)$ and $R(T)$) and magnetization ($M(H)$) measurements(after ref.[59]).

conducting transition temperatures for Ca- and Yb- intercalated graphite are 11.5 and 6.5 K (cf. Fig. 10), respectively, significantly higher than that of the alkali - metal intercalated graphite phases studied before.

Apart from the significant enhancement of T_c, two other aspects immediately attracted attention: In case of of YbC_6 it was initially speculated that $4f$ electrons may play a role and that superconductivity might be mediated by valence fluctuation. This possibility, however, could be ruled out and it was found that Yb, like Ca, is divalent and the f electrons provide no essential contributions to the electronic structure at E_F.[69] The second interesting aspect concerned the role of the so-called 'interlayer band', *i.e.* a three-dimensional nearly-free electron band emerging from electrons localized in the intercalant plane, and its relation to superconductivity together with the conjecture of an unconventional electronic pairing mechanism involving excitons.[70]

This view was questioned based on the results of the first heat capacity study on CaC_6.

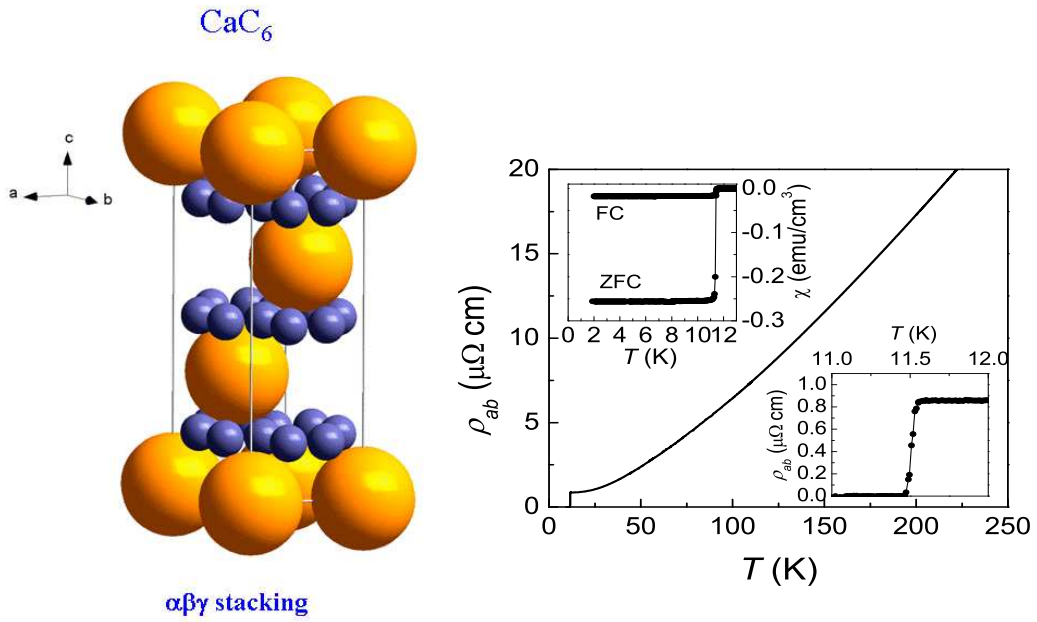

FIG. 10: (left) Crystal structure of CaC_6 (after ref.[67]) and (right) in-plane electrical resistivity and magnetic susceptibility (inset) of CaC_6 (after ref.[68]).

It showed that the anomaly at T_c can be clearly resolved indicating the bulk nature of the superconductivity. In particular, both the temperature and magnetic field dependence of C_P strongly evidence a fully gapped, intermediate-coupled, *phonon-mediated* superconductor without essential contributions from alternative pairing mechanisms.[68]

Linear response calculations provide the following picture of the electron - phonon coupling (cf. Fig. 12): There are three distinct groups of modes, one at $\omega \sim 10$ meV, another around $\omega \sim 60$ meV, and the third located at $\omega \sim 170$ meV which contribute $\sim$0.4, $\sim$0.3, and $\sim$0.1 to the total coupling constant λ. These three groups are mainly composed of the Ca, out-of plane and in-plane C vibrations, respectively. The observed positive pressure dependence of T_c can be understood within this electron - phonon coupling scheme due to a softening of the Ca in-plane phonon modes.[71,72]

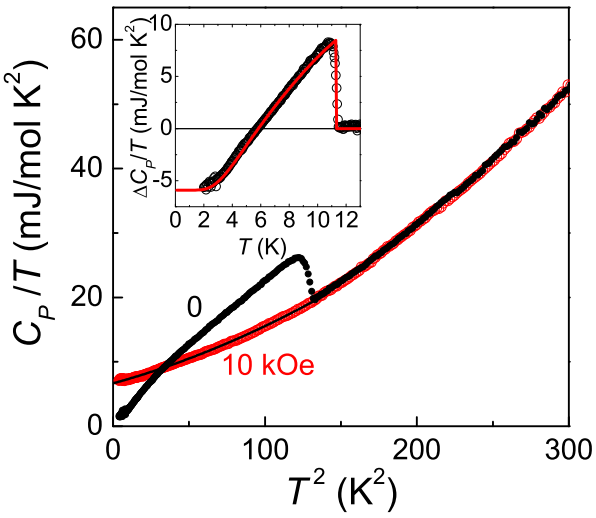

FIG. 11: Temperature dependence of the specific heat of CaC_6 at $B = 0$ and 1 T. the inset shows the temperature dependence of $\Delta C_P/T = C_P/T(B = 0)$ - $C_P/T(B = 1\mathrm{T})$. The (red) solid line is the best fit assuming an isotropic s-wave BCS gap. (after ref.[68]).

IV. CONCLUSIONS

The broad chemical bonding abilities of carbon allowing to realize highly anisotropic chemical structures which together with the low atomic mass of carbon make the modifications of carbon as well as carbon - derived compounds to a wide and rewarding playground to search for new and unusual superconductors.

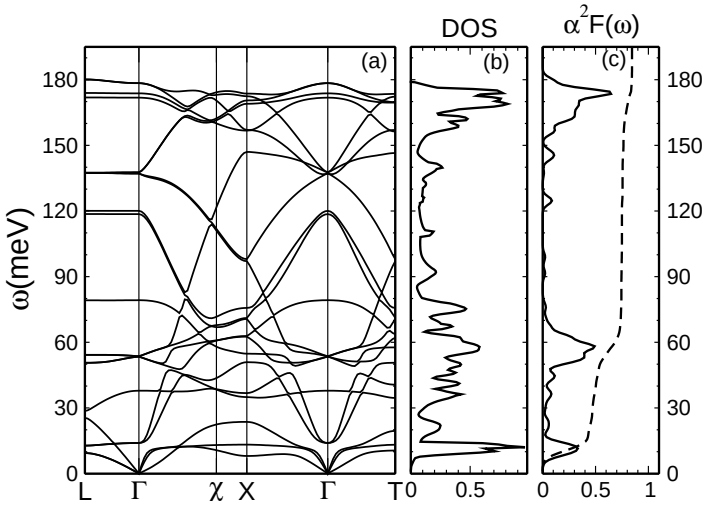

FIG. 12: (a) Phonon frequencies and (b) density of states of CaC_6 along selected directions in the rhombohedral unit cell; the line Γ - X is contained in the graphene planes, while L - Γ is orthogonal to it. (c) Eliashberg function $\alpha^2F(\omega)$ and frequency - dependent electron - phonon coupling $\lambda(\omega)$ (after ref.[72]).

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